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A Summary of Work at the NACA on Flame
Propagation.
By Melvin Gerstein

Presented at the Bumblebee Propulsion
Panel Meeting held November 1, 1951

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As part of a fundamental combustion program at the NACA we have been

studying the ignition, flame propagation, and inflammability limits of various fuel-air mixtures. I will summarize briefly some of the results we have obtained in one phase of this program -- the study of the rate of flame propagation. I will hit only the highlights of this research, since more detail can be obtained from the reports dealing with individual phases of the work. We are interested in studying the rate of flame propagation for two principal reasons. First, the results may have immediate applications in understanding and improving the design of combustors and the selection of fuels, and second, the results may ultimately lead to an understanding of the mechanism of the combustion process which will enable us to predict the properties and behavior of flames. It is the progress toward this second objective that I will review today.

One of the important differences between fuels is the rate at which a flame will propagate through mixtures of the fuel with air. We have studied this rate of propagation through homogeneous mixtures of fuel and air contained in tubes at room temperature and atmospheric pressure (references 1,2,3). From measurements of the speed of the flame, the flame surface area, and the velocity of the gas motion ahead of the flame, burning velocities were obtained which were in good agreement with flame speeds determined by the Bunsen method. Some of these results are summarized in figure 1 where we have plotted the maximum flame velocity against the number of carbon atoms in the molecule. These maxima were determined from curves of flame speed against fuel concentration. Data are shown for paraffins, olefins, cycloparaffins, diolefins and acetylenes. It is readily seen that the paraffins have the lowest flame velocity, the olefins following. The cycloalkanes, containing three or four carbon atoms, fall slightly above the isomeric olefins, while the larger rings compare more closely with the paraffins. The isolated and conjugated diolefins

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are next, while the cumulated diolefins and the acetylenes are at the top of the list, having the highest flame velocities of the hydrocarbon types studied. In general, the differences between the flame speeds of different classes of hydrocarbons are greatest in compounds of low molecular weight, the influence of structure on flame speed decreasing as the molecular weight of the compound increases. Not shown in the figure is the effect of methyl-substitution or branching on flame velocity. In all of the classes of compounds listed here the effect of branching is to reduce flame velocity. A single substituent leads to greater reductions in flame velocity in the diolefin and acetylene families and produces less change in the olefins and paraffins.

While many of the trends shown on this slide follow the general chemical reactivity of these types of compounds, these results can also be used to determine the ability of various theories of flame propagation to predict flame velocities. Although many such theories exist, only a few lend themselves easily to calculation for a large number of compounds. The diffusion theory of Tanford and Pease is such a theory, since one can readily calculate the equilibrium flame temperatures and radical concentrations required (references 4 and 5). The rate constant in the theory is more difficult to obtain. However, if one plots the square root of some active radical concentrations against flame velocity, as we have done in figure 2, a fairly good straight line is obtained. This indicates that the theory applies if the reaction rate expression is assumed constant for the hydrocarbons considered. On this figure only ethylene deviates appreciably, while in other work acetylene and some oxygenated compounds deviate, indicating that a different rate expression is required for these compounds. The agreement with the diffusion theory does not mean, of course, that other theories could not be applied with equally good

results. If we plot in figure 3 flame velocity against flame temperature all of the data except ethylene fall on a single curve. This means that it is likely that any theory strongly dependent on flame temperature would probably correlate the data. In fact, Walker and Wright (reference 6) have recently shown that the Semenov thermal theory can be applied to this data if one uses a constant activation energy for all of the compounds studied except ethylene.

Among the hydrocarbons acetylene with a flame speed of about 140 centimeters per second (reference 7) represents the maximum likely to be reached. Our interest in compounds with very high flame speeds has led us to an investigation of some metallic compounds. It is known that some metallic hydrides and some organo-metallic compounds are spontaneously inflammable, so that it might be expected that some derivatives of these metallic compounds would have high flame speeds and yet not be spontaneously flammable under ordinary handling conditions. In one of our preliminary investigations in this regard we have studied the flame velocities of a series of organo-silanes. Some of our results are summarized in figure 4. Here we have plotted the flame speed against the number of silicon to hydrogen bonds in the compound for three compounds - tetramethylsilane, trimethylsilane and diethylsilane. As the number of silicon to hydrogen bonds is increased, the flame speed increases rapidly. Ethylsilane, not shown on the figure, had a flame velocity above acetylene, although we have not yet obtained a precise value. Methylsilane has a considerably higher flame velocity and on one occasion exploded spontaneously while the silane-air mixture was being prepared. Of course, silane itself SiH_4 is spontaneously flammable.

While we have not yet completed our theoretical study of these compounds, one can make some interesting comparisons between the isomeric compounds,

tetramethylsilane and diethylsilane. The ratio of the flame speed of diethylsilane to tetramethylsilane is about 2, while the ratio of flame temperatures is only 1.02 and the ratio of the square root of the diffusion concentration of radicals is only 1.07. In other words, while the flame velocities differ by 100 percent the flame temperature differs only by 2 percent and the radical concentrations only by 7 percent. It is evident, therefore, that for either a thermal or diffusion theory to apply the major difference between the two compounds must appear in the reaction rate expression. This is a study we hope to make, for it is not unreasonable to expect that the reactivity will be strongly affected by the number of silicon to hydrogen bonds in the molecule.

When compounds with high flame speeds are found, one asks the inevitable question "Will a few drops added to a gallon of gasoline result in a super fuel?". In the past the answer has been no, and I am afraid the answer is still no for the silanes. In figure 5 we have plotted flame speed against the concentration of diethylsilane in normal pentane. These compounds require the same amount of oxygen per mole of fuel since they differ only in that the silane contains one silicon atom in place of a carbon atom. The curves indicate that the blending is poorer than one might expect from a linear blending relationship, and significant increases in flame velocity occur only when the mixture contains an excess of 25 percent diethylsilane.

Up to this point I have been discussing the role played by the fuel in the propagation process. Equally important, of course, are the experimental conditions such as the temperature and pressure of the mixture and the nature of the oxidant. Let us first consider the effect of initial mixture temperature on flame velocity. I would like to discuss some of Mr. Dugger's research along these lines (references 9, 10 and 11). He has determined the effect of initial mixture

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temperature on the flame velocities of methane, propane and ethylene using the Bunsen burner technique. The results are summarized in figure 6 where flame velocity is plotted against initial mixture temperature. The methane curve covers a temperature range from -132°C to 342°C . The propane and ethylene from -73°C to 343°C . These curves extend over practically the entire range of flammability for the fuels, since the fuels would condense at lower temperatures while the mixtures would react spontaneously at higher temperatures. It is possible to compare these results with the effect of temperature on flame speed which would be predicted by either a thermal or diffusion mechanism. In order to make the comparison the temperature dependence of the various terms in the equations was evaluated. The remaining constants in the equation were evaluated by setting the theoretical flame speed equal to the experimental at one point - room temperature. The variation of flame velocity with temperature from this point serves as a test of the theory. A typical comparison is shown in figure 7. The experimental curve is shown as the dotted line. The curve predicted by the thermal theory of Semenov assuming a bimolecular mechanism is shown as a solid line and the curve predicted by the diffusion theory of Tanford and Pease is also shown as a solid line. It is evident that both theories predict the effect of initial mixture temperature on flame speed with satisfactory precision. Similar curves were computed for methane and propane. In all cases it was found that the theoretical curves computed by either theory were within 20% of the experimental curve. The thermal theory usually predicting slightly higher results while the diffusion theory predicted lower results at high temperatures.

Another relationship has been found between flame velocity and active radical concentrations which emphasizes the importance of diffusion in flame the

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propagation and, at the same time, suggests a means of establishing the temperature dependence of the flame speed of a fuel from the determination of only two points. On the next slide we have plotted flame velocity against the first power of the summation of H, OH, and O radical concentrations multiplied by relative diffusion coefficients. In each case methane, propane and ethylene straight lines are obtained over the entire temperature range studied. While the full significance of this relationship has not yet been determined, it does serve as a simple method of finding the flame speed - temperature variation for fuels showing this linear relationship. The generality of this correlation is not yet known, since it has been applied only to these three fuels.

Increasing the initial mixture temperature results in higher flame temperatures and higher flame velocities. Increasing the oxygen content of the combustible mixture, while holding initial temperature constant, serves the same purpose. We are currently studying the effect of oxygen enrichment on the flame speeds of some representative hydrocarbons. I will discuss the results recently obtained with isooctane using the Bunsen burner technique to measure the flame velocities (reference 12). In order to maintain a gaseous mixture the data were obtained at temperatures slightly above room temperature. Oxygen-nitrogen mixtures were prepared in the range from 15 percent oxygen to 50 percent oxygen. The 21 percent oxygen points were made with air. The results are summarized in figure 9 where we have plotted maximum flame velocity against percent oxygen. A linear relationship is obtained over the range of oxygen concentrations studied for both initial temperatures. Since these data have just been obtained, we have not yet been able to assess the importance of this result in terms of the propagation theories. The necessary calculations are now in progress.

For engineering uses it is possible to combine the effects of temperature and oxygen concentration into a single empirical equation. We had previously found that for limited temperature ranges a log-log plot of initial temperature vs. flame speed was linear. Combining this with the linear relationship shown on this figure we get the empirical relationship shown in figure 10. We have here the experimental flame speed plotted against the flame speed calculated by the equation $U_f = CT_0^n \times (\alpha - 12)$ where U_f is the flame speed, C is a constant equal to .000718, T_0 is the initial temperature, n is a constant equal to 1.5, and α is the oxygen concentration in volume percent. The line drawn in the figure is a 45° line representing perfect correlation. It is evident that this empirical relationship fits the data well. It is interesting to note that the equation predicts 0 flame speed at oxygen concentrations below 12 percent for the mixtures studied. While this may vary with experimental conditions somewhat, it is in close agreement with work we have done on the effect of oxygen concentration on the flammability limits of isooctane (reference 13). These results indicate that no flame will propagate at oxygen concentrations below 10-12 percent. This brings to mind considerations of the earlier thermal theories in which it was believed that the flammability limits occurred at 0 flame speed, although since that time contrary arguments have been raised. Nevertheless, a true mechanism of flame propagation should apply not only to the velocity of propagation but to the limits of propagation as well. Recent work has indicated that the propagation limits might be the result of surface quenching of the flame reactions so that the flame velocity might be expected to be related to quenching distance. This is bound to be true in some instances and, as shown in figure 11, if we plot flame velocity against the reciprocal of the critical tube diameter or quenching distance, a straight line is obtained.

(Reference 14)

In a paper to be published soon by Simon and Belles (reference 15) a mechanism for the quenching of flames based on the destruction of active particles on the walls is proposed. Let us consider a flame propagating in a tube as shown in figure 12. The diffusion mechanism of propagation suggests that the flame progresses into the unburned gas by the diffusion of active radicals. In such a theory the rate of propagation depends strongly on the number of active radicals entering the unburned gas. If some radicals are destroyed by the walls of the container, it is not unreasonable to expect that a condition can be reached in which there are too few radicals for flame propagation. In other words, the reaction is quenched. The number of radicals reaching the wall in such an idealized picture can be computed by an equation developed by Semenov. Such a computation results in the following expression for critical tube diameter:

$$d_1 = \left[\frac{32 A P}{N_f \frac{P_1 k_1}{D_1}} \right]^{\frac{1}{2}}$$

where d_1 = critical tube diameter

A = fraction of gas phase molecules which must react

P = total pressure

N_f = number of fuel molecules per cm^3

P_1 = partial pressure of active particle

k_1 = specific rate constant for reaction of radical with fuel

D_1 = diffusion coefficient of active radical

This equation quantitatively describes the effect of pressure on the quenching distance of propane-air flames as well as the ratio of quenching

distances in tubes and in parallel plates.

The Farford and Pease expression for flame velocity using the same symbols as above is

$$U_f = \left[\sum_1 k_1 P_1 D_1 \frac{nM_c}{PQ B_1} \right]^{\frac{1}{2}}$$

where U_f = flame velocity

n = moles of combustion product per mole of fuel

Q = mole fraction of potential combustion product

B_1 = term arising from radical recombination in gas phase

Combining these equations we get

$$U_f = \frac{1}{a_1} \left[\left(\frac{32nA}{U B_1} \right) \left(\frac{\sum k_1 P_1 D_1}{\sum \frac{nM_c}{PQ B_1}} \right) \right]^{\frac{1}{2}}$$


For the propane-air mixtures studied the term in the brackets is almost a constant so that the theoretical relationship agrees with the correlation shown in the figure.

Thus far my discussion has centered on hydrocarbon fuels and the application of approximate theories of propagation to the prediction of flame velocities. The complex nature of the combustion of hydrocarbons makes it almost impossible to treat their flames exactly. As you know, Hirschfelder and Curtiss have recently developed an exact theory of flame propagation which includes the expressions for diffusion, heat transfer and chemical kinetics. This theory also becomes difficult to solve for chemical reactions of a complex nature, but Hirschfelder and co-workers have applied the equation to the calculation of flames resulting from uni-molecular and bi-molecular reactions. One flame they have treated in detail is the uni-molecular decomposition of acetylene. We have been studying this flame experimentally (reference

16).

Our first experiment was directed to determine if a flame could be propagated through pure azomethane at room temperature and atmospheric pressure without detonation. The theory predicted a fast flame, but much of the literature indicated a detonation might occur. Consequently, we filled a one-inch tube two feet long with azomethane at atmospheric pressure. The flame was initiated by means of a heated wire. While it was evident a very fast flame had propagated, no detonation occurred. No visible radiation could be observed during the progress of the flame, so that later experiments were performed in tubes of rectangular cross section and were observed by the shadowgraph technique. To reduce the velocity of the flame a mixture containing only about 16.7 percent azomethane in oxygen-free nitrogen was studied. The flame was photographed by means of a motion-picture camera. A typical frame is shown in figure 13. The flame front closely resembles a hydrocarbon-air flame. A spatial velocity of 56 centimeters per second was determined from timing marks on the film and distance marks on the tube. A normal burning velocity of 20 centimeters per second was computed from this value. The theory predicted a flame velocity of only about 1 centimeter per second. While the difference between the experimental value of 20 and the theoretical value of 1 may seem discouraging, it must be remembered that low temperature kinetics was used. While the 16.7% azomethane mixture has a fairly low flame temperature, it is still considerably above the usual range for decomposition studies. A 20 percent reduction in activation energy from the 50 kilocalories determined by low temperature studies to a value of 40 kilocalories then the theory comes into agreement with the experiment.


Another uni-molecular decomposition which is known to result in a flame is the decomposition of ethylene-oxide. We have recently studied this system



theoretically and experimentally (reference 17). The results of the calculation were based on the recently published kinetics for the decomposition by Walters and Mueller. There is fairly good agreement among various investigators on the activation energy for this reaction, the values falling between 52 and 54 kilocalories per mole. The flame temperature is not known quite as precisely. Using extreme values for the heat of reaction flame temperatures vary from 1460° K to 1600° K. Since the activation energy and flame temperature appear in exponential form, in the flame velocity equations, the effect of changes in these parameters on the computed flame velocity was determined. ~~THESE~~ Figure 14 shows the variation of flame velocity with activation energy. The extreme values of activation energy taken from the literature are shown by the arrows and would produce a flame velocity variation from 12 to 16 centimeters per second.

The effect of flame temperature on flame velocity is shown in figure 15. Again, flame velocity is plotted against flame temperature and extremes in flame temperature are shown by the arrows. The range of temperatures from 1460° to 1600° would produce flame velocities varying from 12 to 29 centimeters per second.

In the experimental study several attempts were made to obtain a stable Bunsen flame of the ethylene-oxide decomposition. While ignition could be easily accomplished, by means of a hot wire, a stable flame could not be obtained even in experiments where ethylene oxide was preheated to 200° C. In experiments performed in tubes the flame would propagate upward and horizontally but downward propagation could not be obtained. Since the flame had no visible radiation, shadow motion pictures were taken.



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A typical photograph of an ethylene-oxide flame traveling horizontally is shown in figure 16. Note that the flame does not touch the bottom of the tube, actually filling only about one-half the cross section. Note also the long trailing edge of the flame.

A typical flame traveling upward is shown in figure 17. This flame is much more symmetrical than the other, and fills the tube cross section. The spatial flame velocity obtained from the films was found to be 25 centimeters per second in both cases. From this a normal burning velocity of 12 to 16 centimeters per second is determined. This is in good agreement with the theoretical values of 12 to 29 centimeters per second.


Although this is extremely encouraging, it must be pointed out that some uncertainty exists about both the measured and calculated values. The results of both this and the acetylene experiments indicate that the Hirschfelder-Sartorius theory of flame propagation merits further investigation, both theoretically and experimentally.


In conclusion, I would merely like to mention that we are continuing research in many of the areas of flame propagation I have mentioned today as well as extending our work to include heterogeneous and turbulent conditions.

Melvin Gerstein



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SUMMARY OF FLAME VELOCITIES

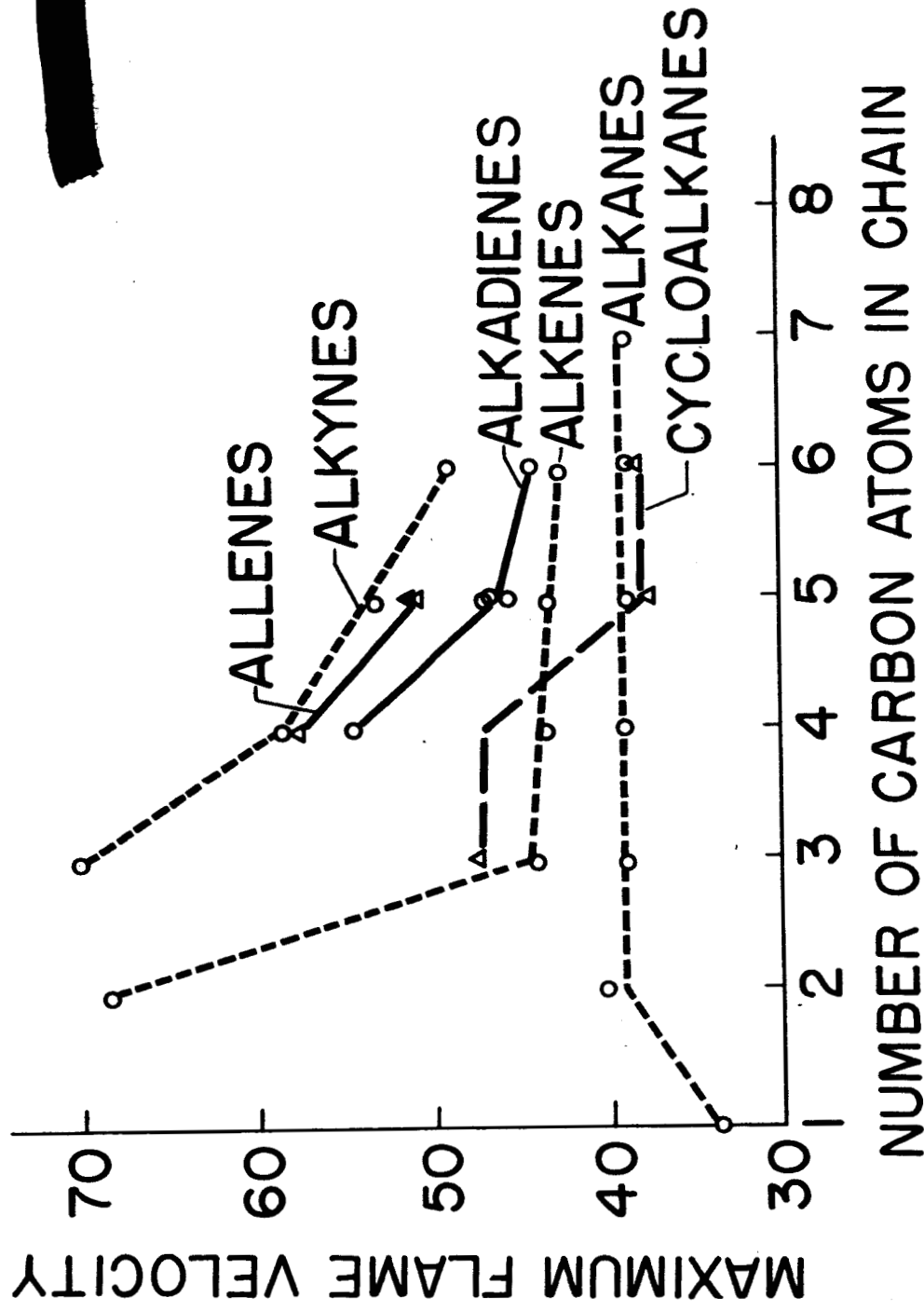


Figure 1



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CORRELATION WITH THE SQUARE ROOT LAW

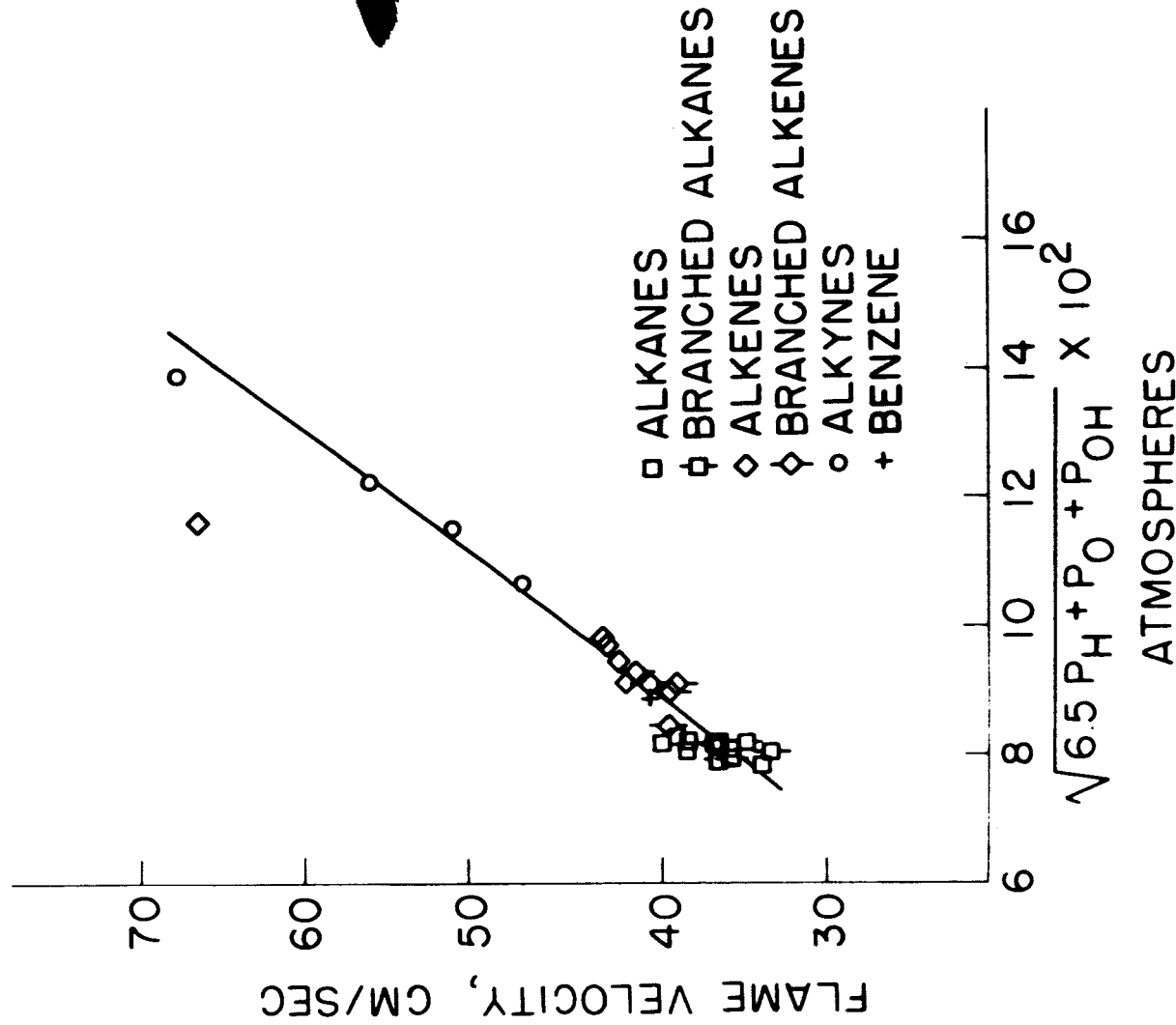


Figure 2



VARIATION OF FLAME VELOCITY WITH EQUILIBRIUM FLAME TEMPERATURE

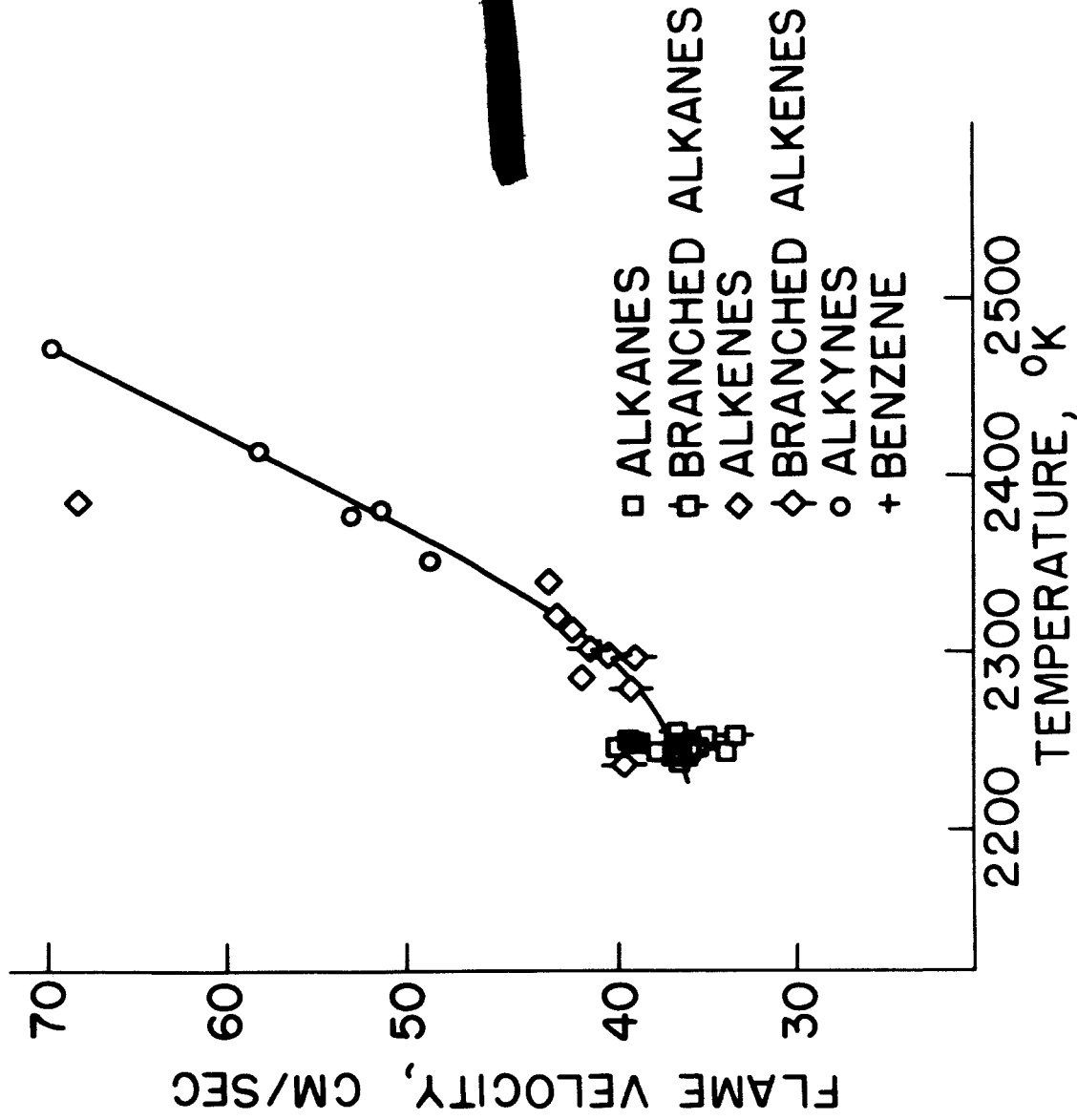


Figure 3



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EFFECTS OF SUBSTITUTING HYDROGEN ATOMS WITH ALKYL GROUPS

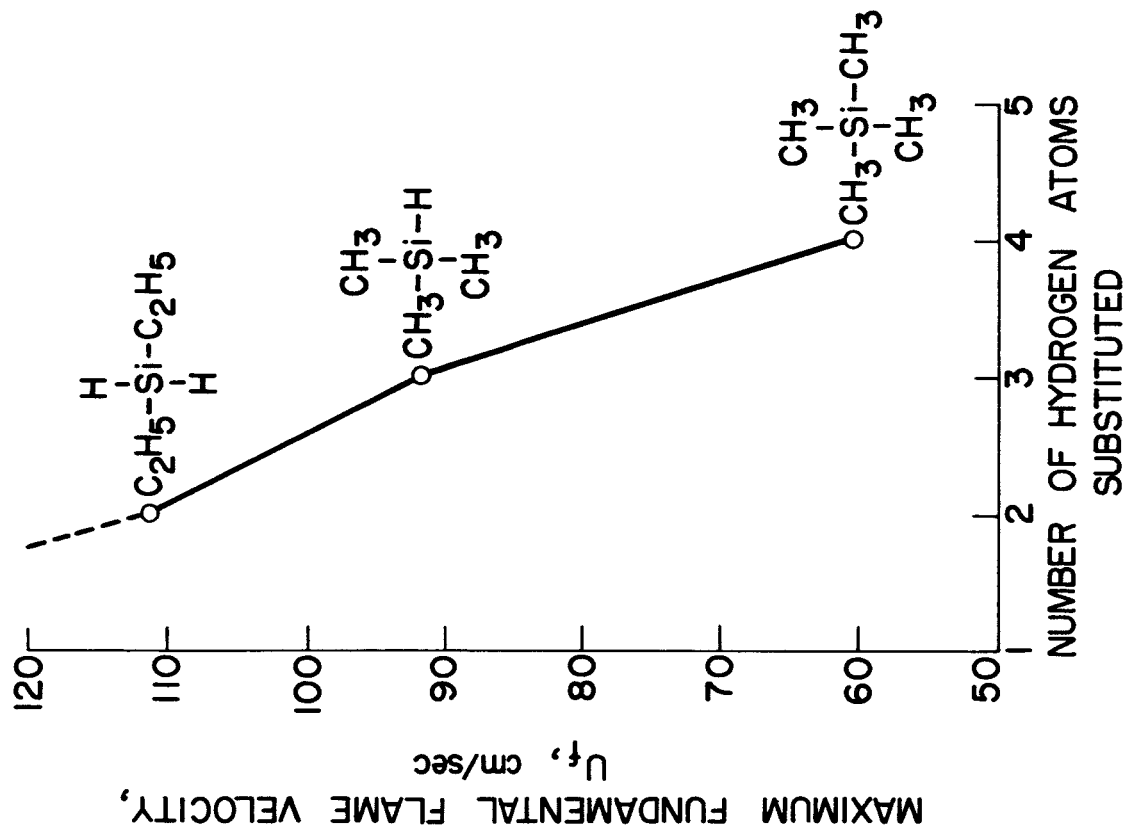


Figure 4



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FUNDAMENTAL FLAME VELOCITY OF DIETHYLSILANE-PENTANE-AIR MIXTURES

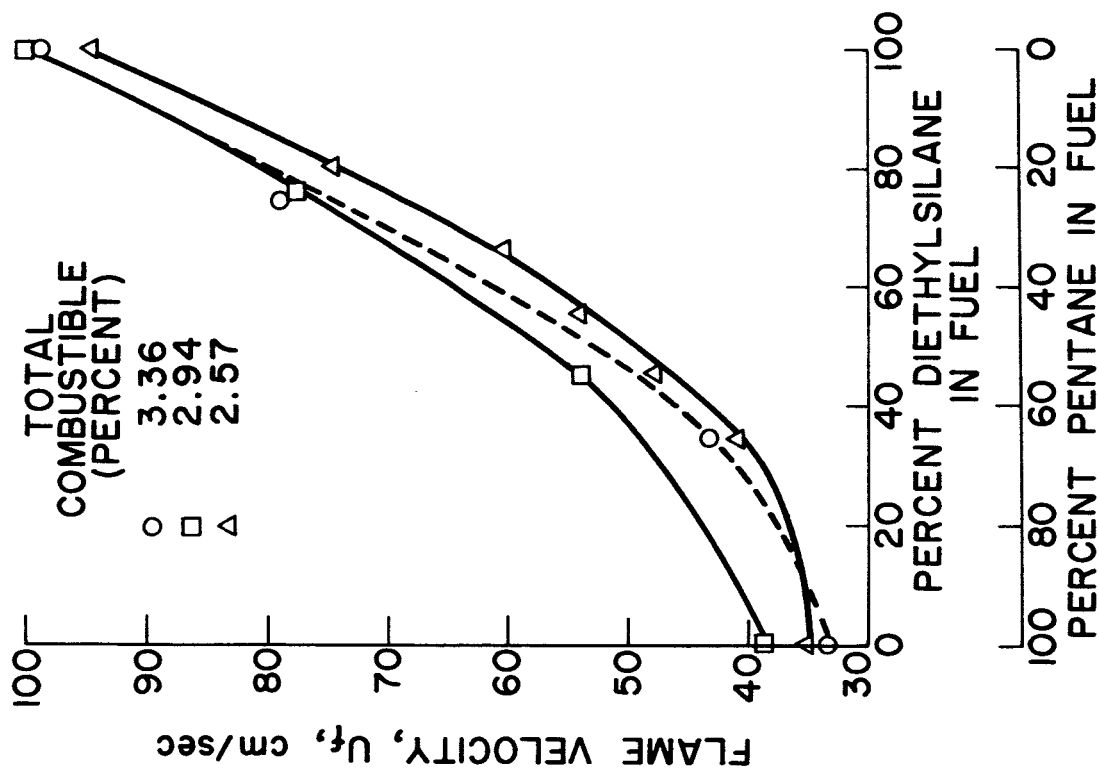


Figure 5

EFFECT OF INITIAL TEMPERATURE ON MAXIMUM FLAME SPEED

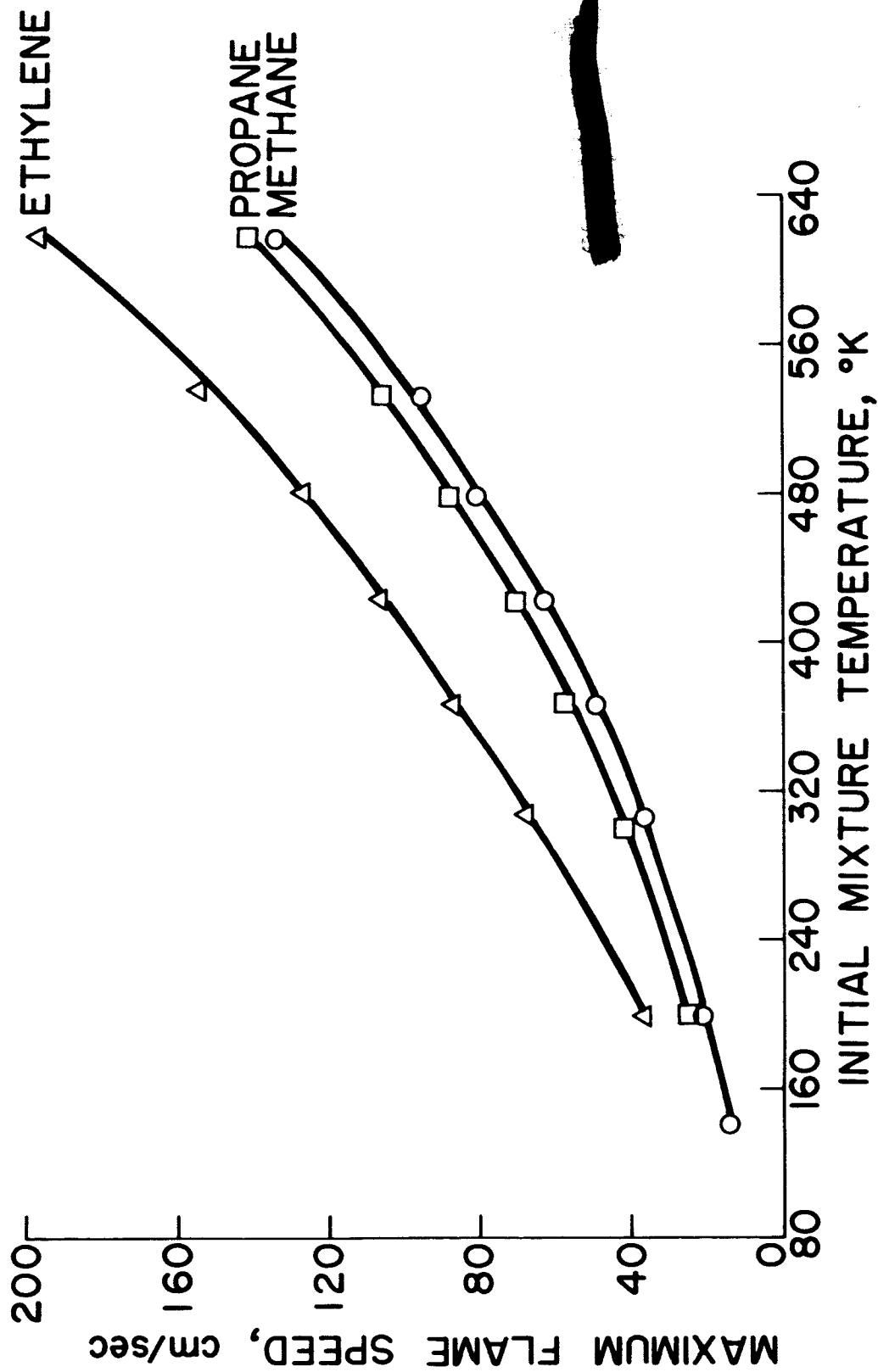


Figure 6



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COMPARISON OF THEORETICAL AND EXPERIMENTAL CURVES

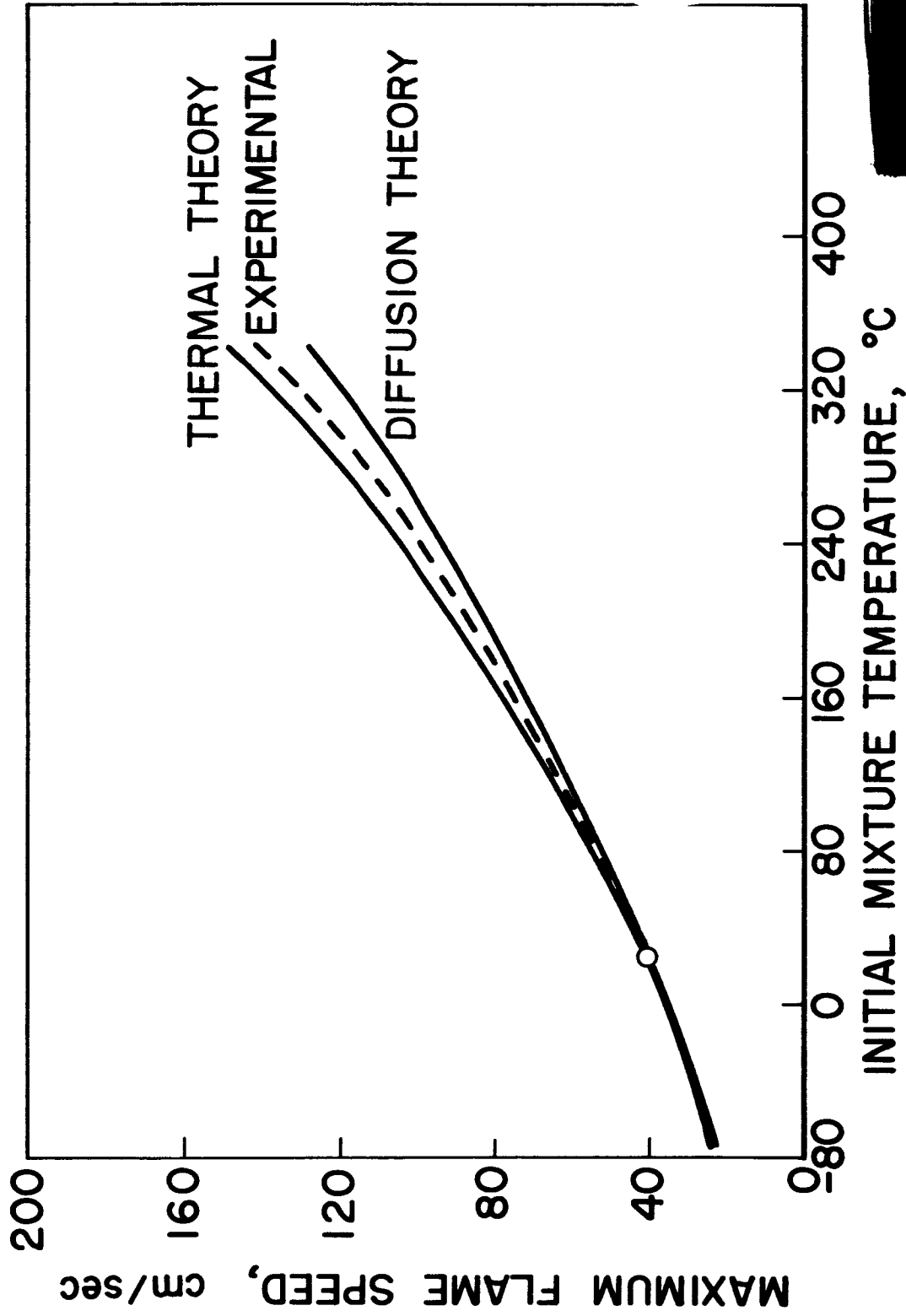


Figure 7



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VARIATION OF FLAME SPEED WITH RADICAL CONCENTRATIONS

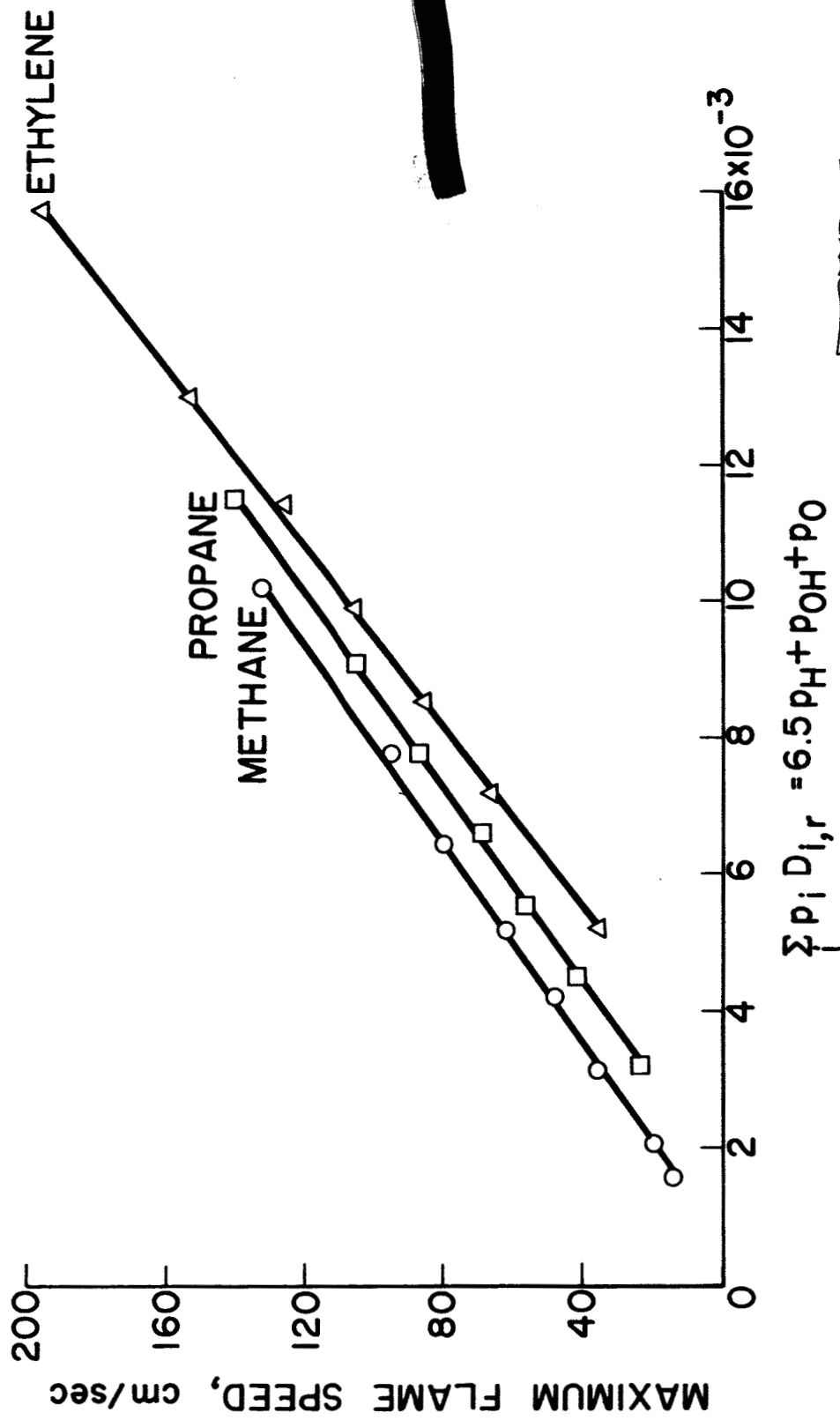


Figure 8

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EFFECT OF OXYGEN CONCENTRATION ON
FLAME SPEED

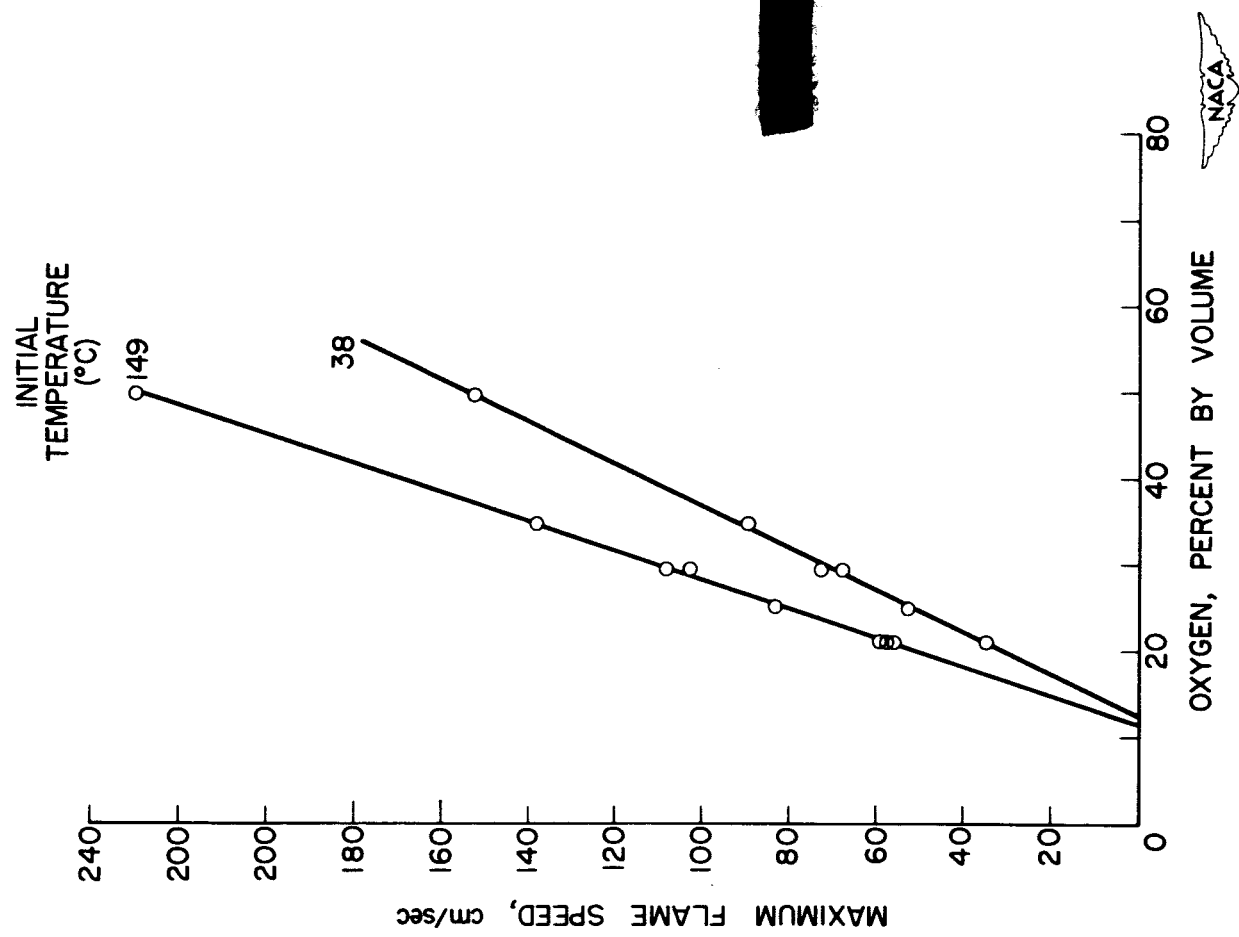


Figure 9

EMPIRICAL CORRELATION OF FLAME SPEEDS

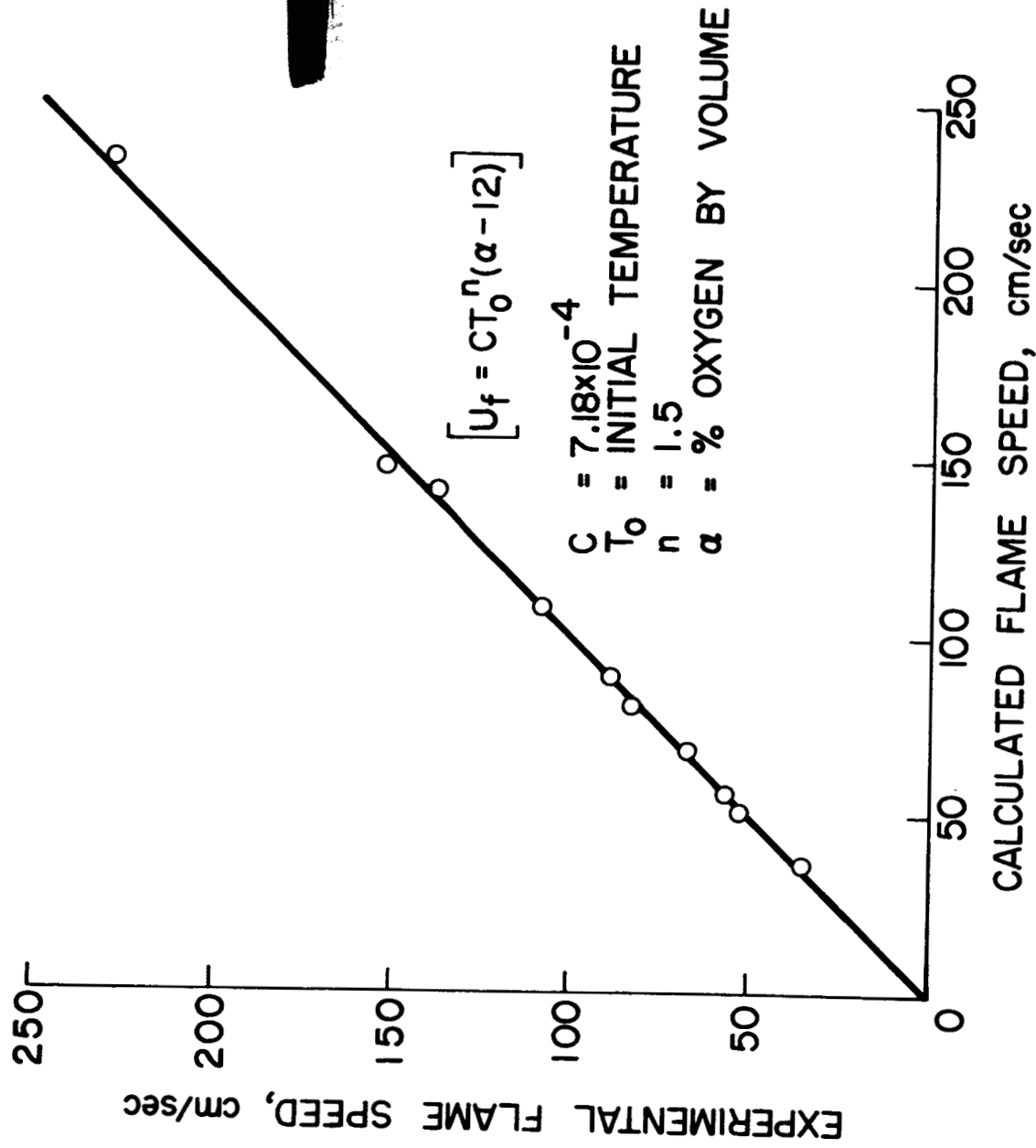


Figure 10



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CORRELATION OF FLAME SPEED WITH MINIMUM SLIT WIDTH AT VARIOUS TEMPERATURES FOR PROPANE-AIR MIXTURES

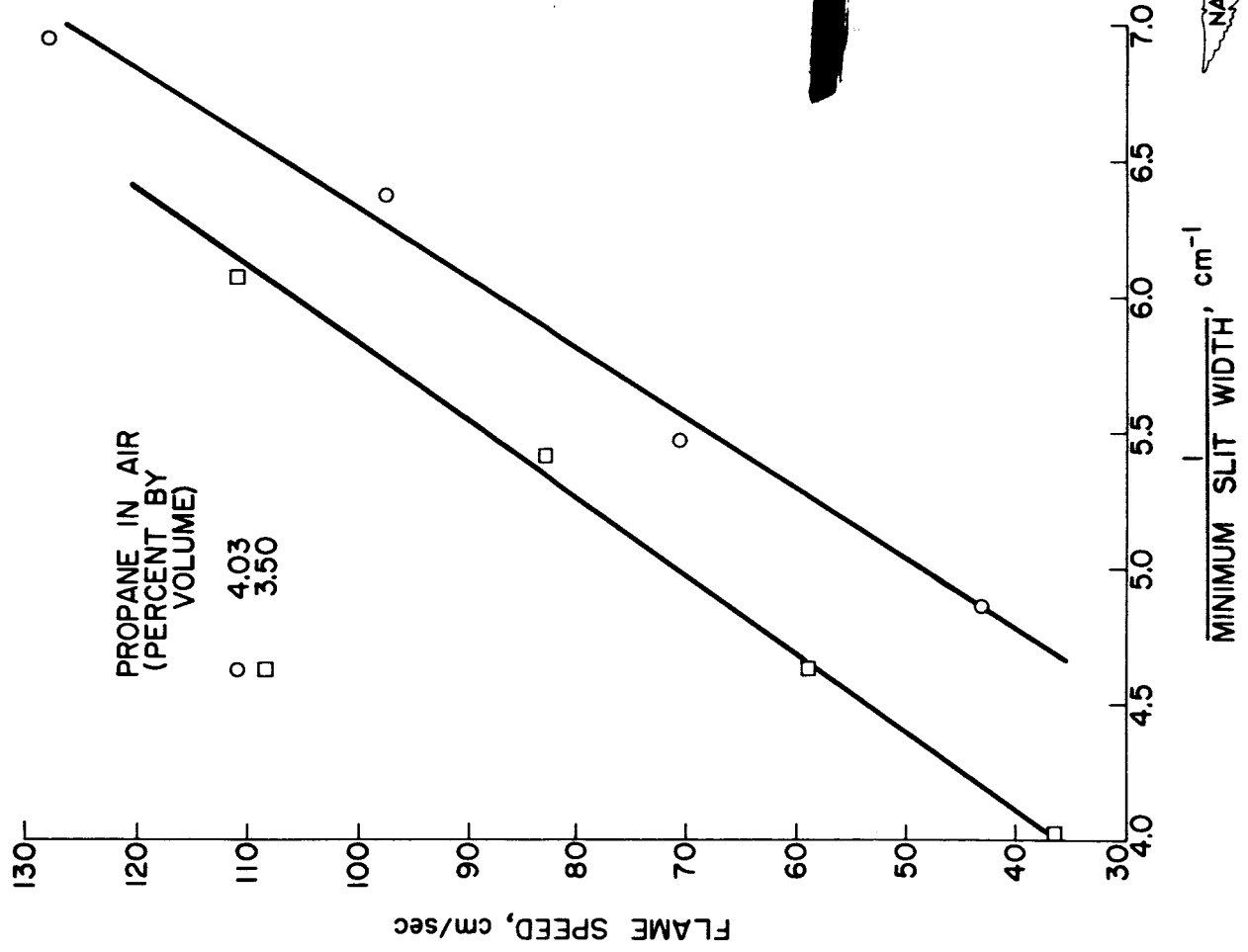


Figure 11



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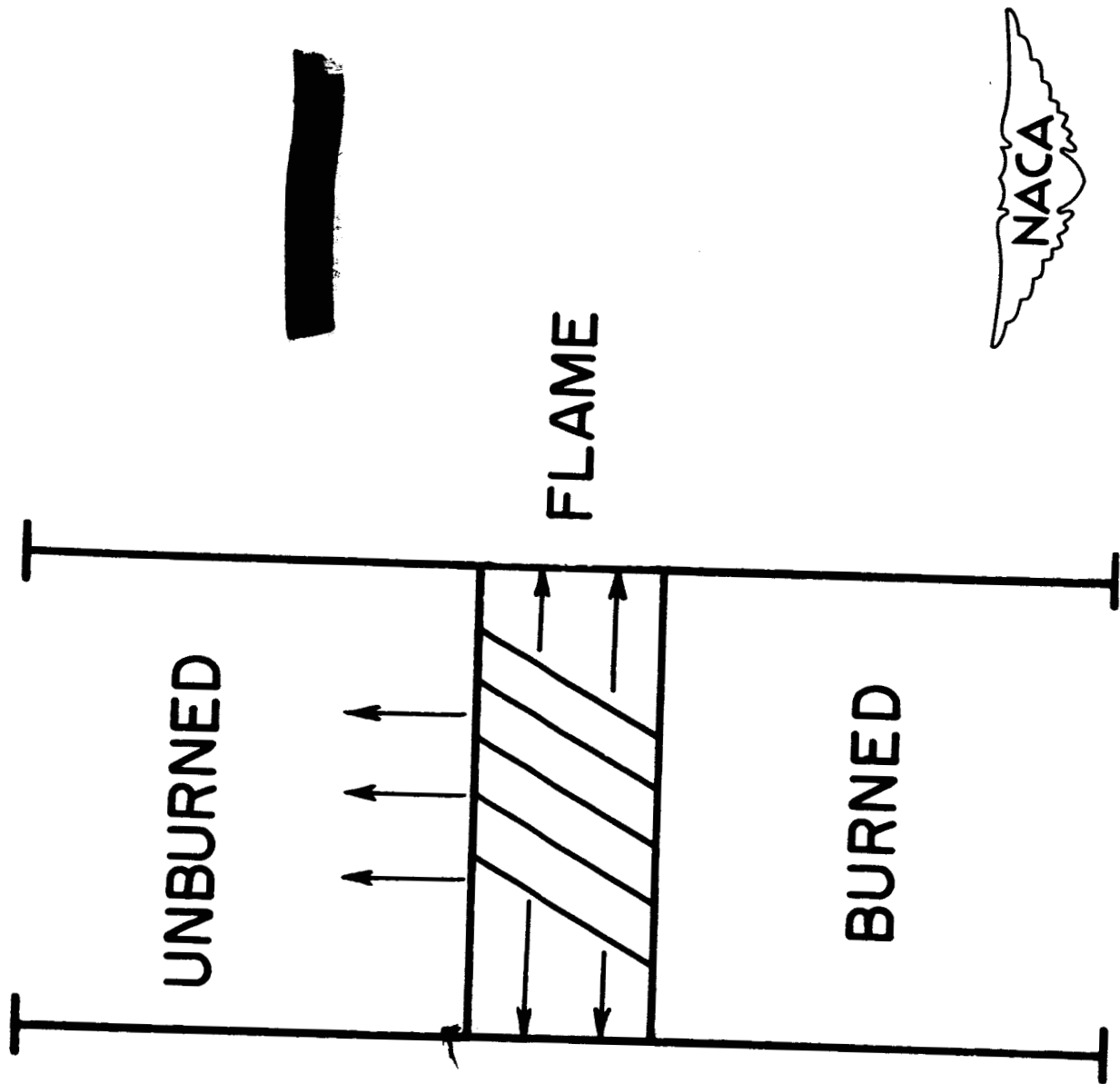


Figure 12

SHADOW PHOTOGRAPH OF FLAME



Figure 13

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CALCULATED FLAME VELOCITY VS.
ACTIVATION ENERGY

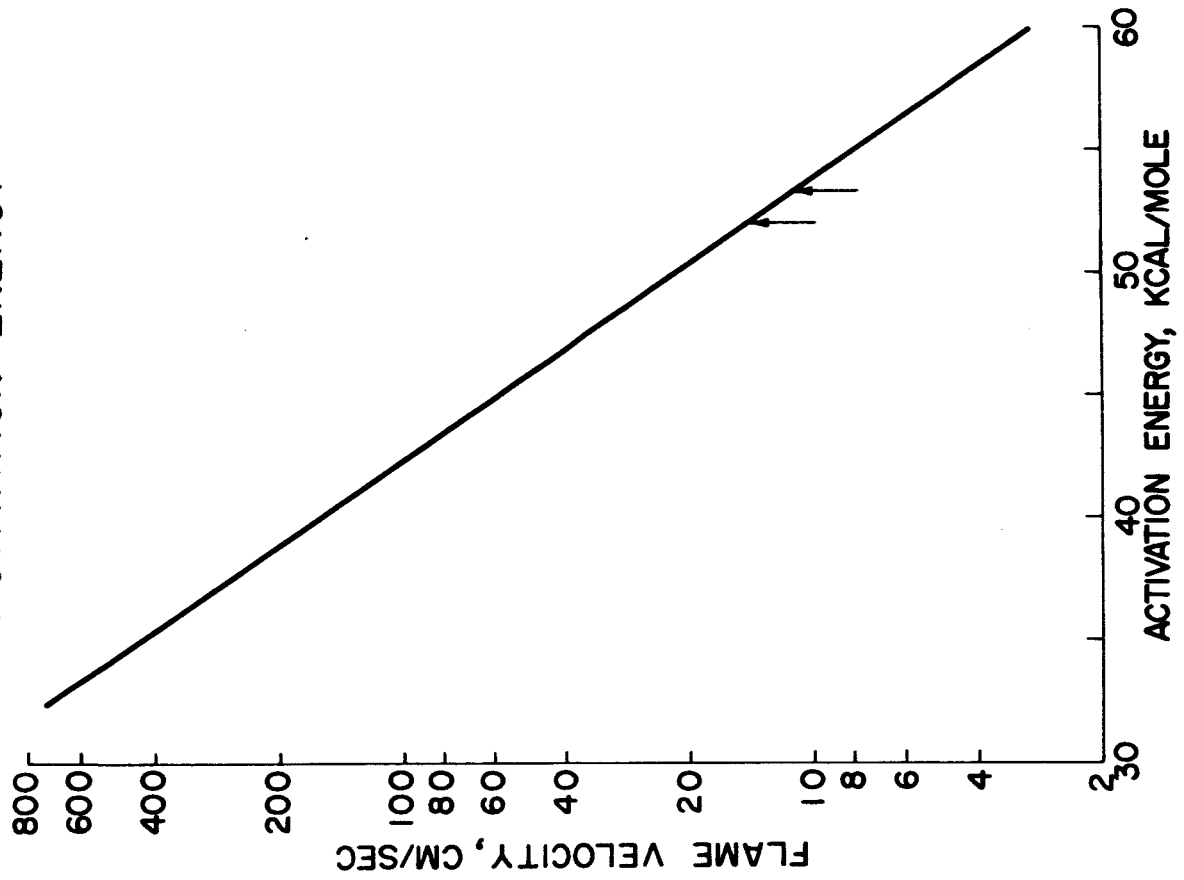


Figure 14

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CALCULATED FLAME VELOCITY VS. FLAME TEMPERATURE

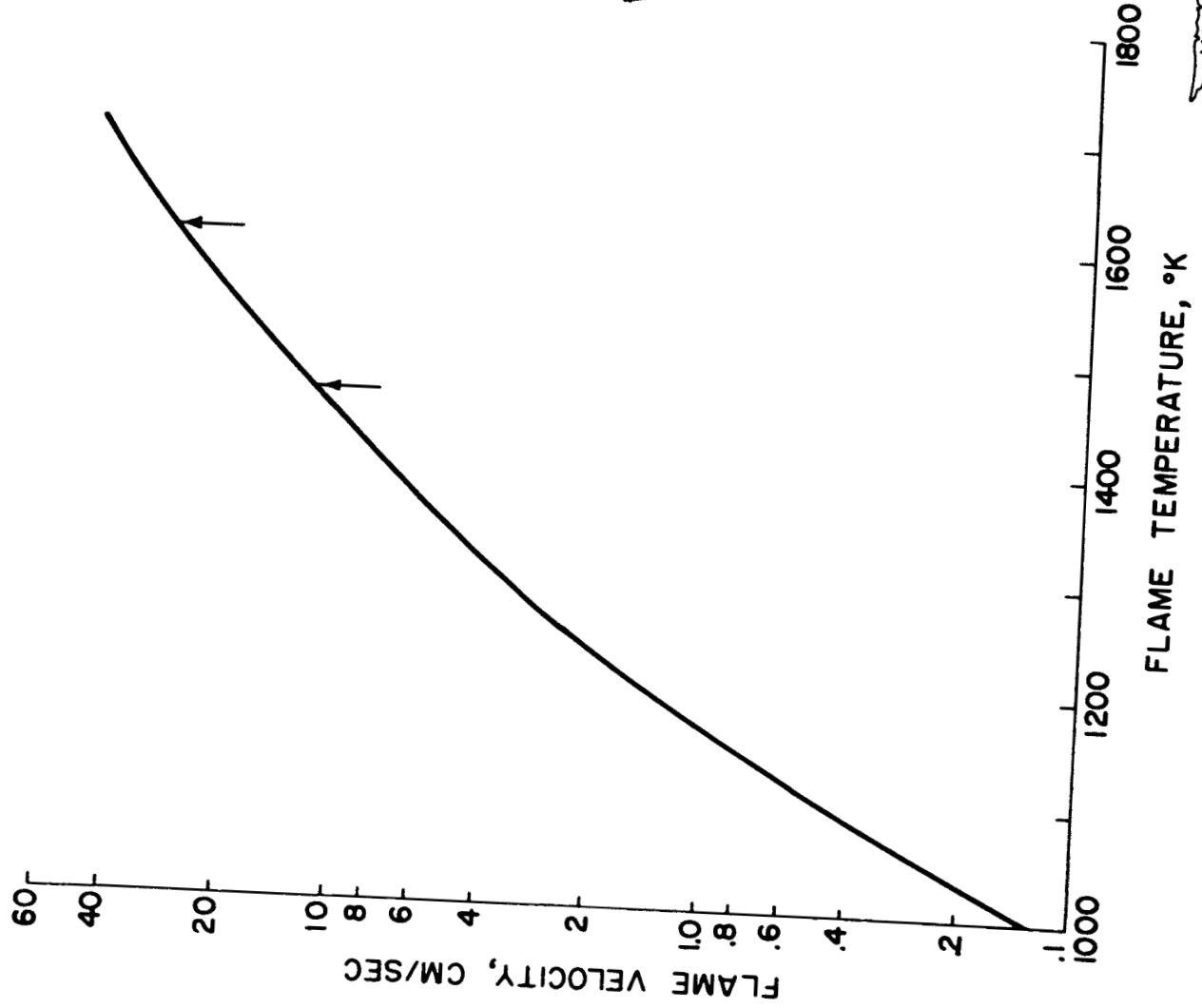
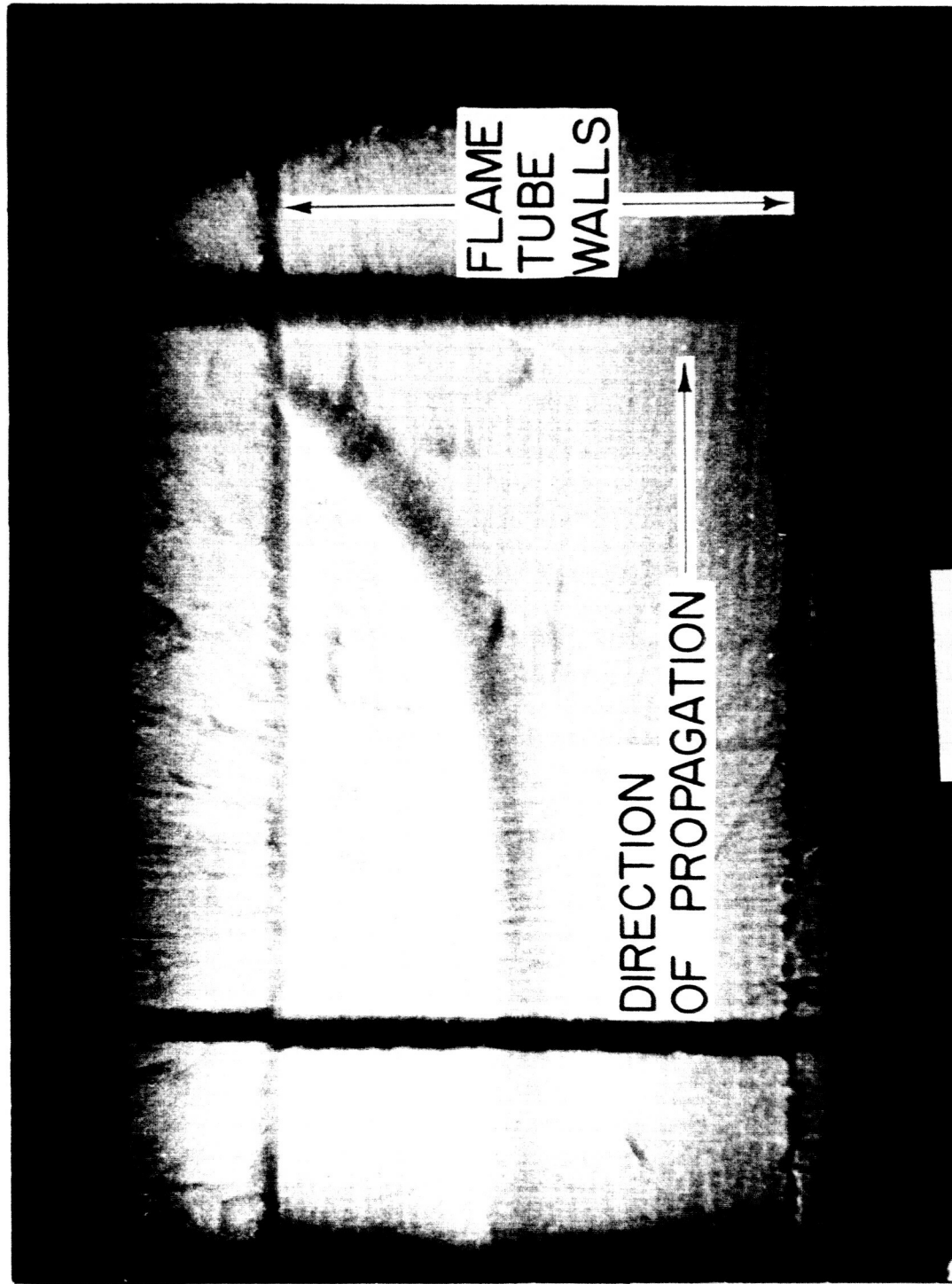


Figure 15

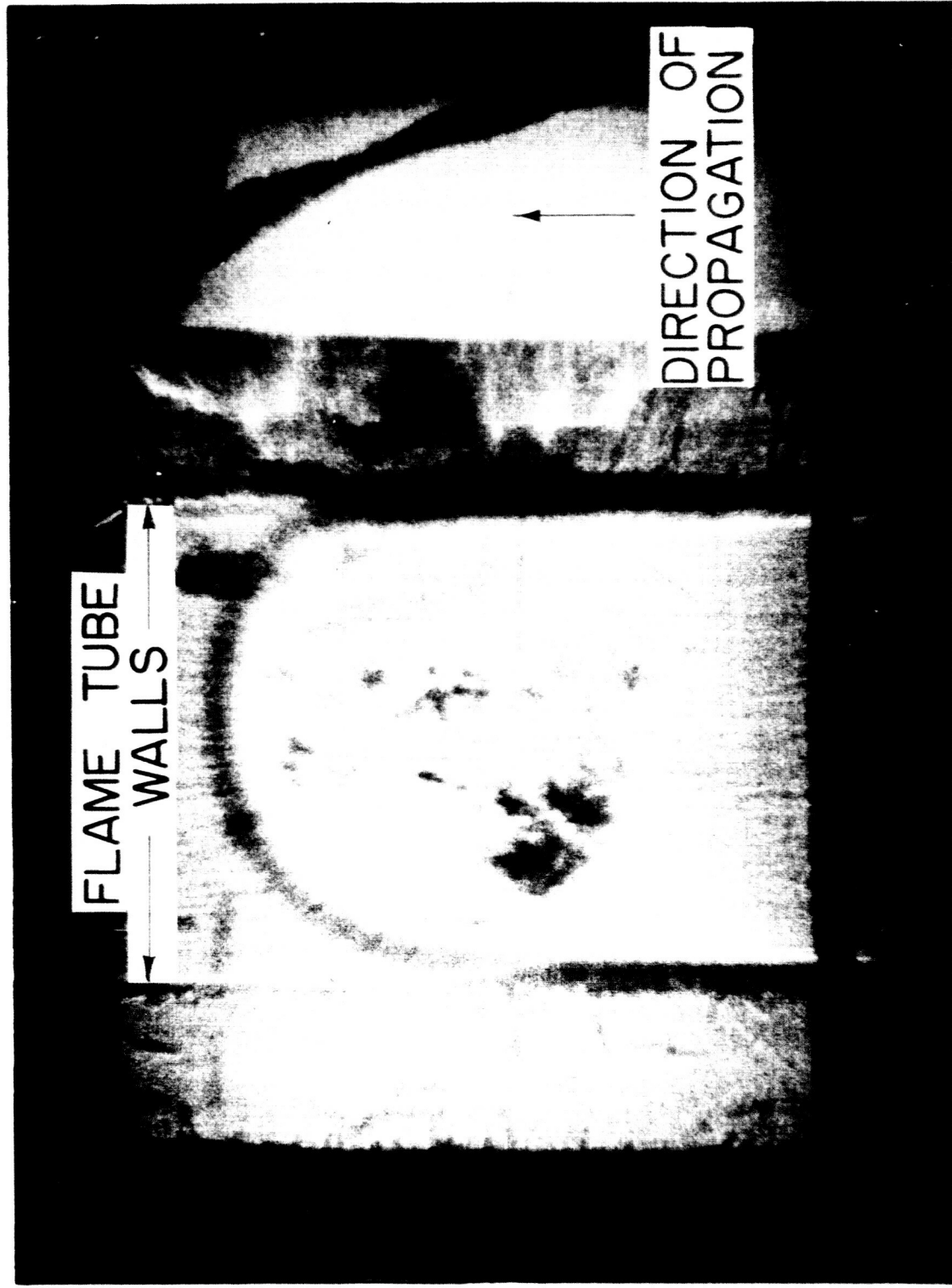
SHADOW PHOTOGRAPH OF FLAME IN HORIZONTAL PROPAGATION



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Figure 16

SHADOW PHOTOGRAPH OF FLAME IN UPWARD PROPAGATION



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Figure 17